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Viscous Liquids and the Glass Transition: A Potential Energy Barrier Picture

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Recent attempts have been made to assess the relative merits of the free volume and entropy theories of viscous flow in glass-forming liquids by accurate measurement of viscosity over wide temperature ranges, and subsequent comparison with the equations derived from these theories. In the author's view, this effort is misguided. The theories are crude and qualitative, and such tests are too stringent. It is better to make qualitative or semiquantitative comparison of a wide variety of physical phenomena; judged by this criterion, the entropy theory appears more successful. It is conjectured that further progress can be made by accepting the crude, naive character of any model we are likely to find tractable for the foreseeable future, and recognizing both the values and limitations of such models. A picture of the flow process in viscous liquids is proposed, in an attempt to answer certain questions about the molecular steps in flow either answered unsuccessfully or ignored by present theories, in the hope that it will lead a model closer to molecular reality but still sufficiently tractable to allow some range of predictive value. The model is based on the idea that in "viscous" liquids (shear relaxation time $\geq 10^{-9}$ sec) flow is dominated by potential barriers high compared to thermal energies, while at higher temperature, this will no longer be true. Certain concepts borrowed from the continuum theory of lattice defects are joined to a qualitative description of viscous flow due to Orowan, to provide a picture which leads to some qualitative predictions about flow and relaxation in the liquid and glassy states.

I. INTRODUCTION AND CRITIQUE OF PRESENT THEORIES

It is now widely recognized that the occurrence of a glass transition is an almost universal property of matter in the liquid state. In addition to the mixtures of inorganic oxides that make up what is called "glass" in common speech, glasses are formed by organic polymers,[1] molecular liquids such as glycerine, glucose, or toluene,[2,3] fused salts,[4–6] and some metallic systems.[7–10] So far none of the noble gas liquids have been produced as glasses, but it is interesting to note that in molecular dynamics "experiments" on spherically interacting particles performed by computers, it is very hard to make the systems "crystallize" on decrease of temperature or increase of density.[11] Experiments on metal spheres as models of particles give similar results.[12]

The classic explanation of glass formation is that if a liquid is cooled, without crystallization intervening, to a sufficiently low temperature, the increase of viscosity with decrease of temperature causes it to reach a state of such high viscosity that it acts effectively like a solid.[13,14] Although there are various theories of the glass transition that assign to it a thermodynamic character, there does not appear to be appreciable disagreement with the view that the above explanation is correct for the experimentally observed transitions. In what follows, the interesting question of why crystallization does not intervene will be disregarded, and the passage from the liquid to the glassy state will be assumed. It will be noted that the basically relaxational character of the glass transition implies a shear modulus G for a liquid, as well as a shear viscosity η_s, a property readily studied by acoustic measurements.[15] It would appear then that a theory of the glassy state will be a byproduct of a theory of liquid viscosity. Here we are up against the difficulty that we do not as yet have a theory for the viscosity of the simplest liquids, based solidly on principles of molecular dynamics, though there is hope we are not too far from one.[16] We are certainly far from having a molecular theory for the overwhelming majority of liquids, whose molecules have unsymmetrical force fields. The types of theories proposed for the viscosity of those liquids known experimentally to be glass formers are necessarily quite crude, depending more on physical intuition than physical or mathematical rigor. There are two that have some degree of general acceptance at the present time: the free-volume theory, first proposed by Williams, Landel, and Ferry,[1,17] and subjected since to a number of revi-

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sions and modifications,[18–20] and the entropy theory of Gibbs and associates.[21–25] These two theories, in the form in which they were originally put forward, predict about the same sort of temperature dependence of viscosity near the glass transition temperature T_g, both agreeing fairly well with an empirical equation proposed independently by Vogel,[26] Fulcher,[27] and Tammann and Hesse[28]:

$$\ln\eta = \ln\eta_0 + [A/(T-T_0)].$$

T_0 in the above is an experimentally determined parameter having the dimension of temperature. $T_0=0$ corresponds to what is usually referred to as "Arrhenius behavior" of the viscosity. Critical comparisons between these two theories have been made in a number of ways. First of all, and most obvious, the effect of pressure on viscosity or on T_g has been studied. In this most crucial experiment the free volume theory fails badly: the entropy theory, on the basis of limited and uncertain data, gives the correct answer.[29,30] Second, in the glass transformation range, the effect of the thermodynamic and kinetic contributions to relaxation can be separated, as the system may be studied out of equilibrium, and the relative importance of the thermodynamic state (volume or entropy) and of temperature may be evaluated. Here again the free volume theory fails badly for most glass-forming liquids.[31,32] The entropy theory has not been critically examined, but it gives at least qualitatively the correct answer, in allowing for a direct effect of temperature.[33] (The above two conclusions are based on the original formulation of the free volume theory by Williams, Landel, and Ferry,[1,17] in that the free volume fraction is assumed to be frozen in at T_g and undergo no additional change on further cooling. Its pressure and temperature dependence above T_g are measured then by $\Delta\beta=\beta_l-\beta_{gl}$ and $\Delta\alpha=\alpha_l-\alpha_{gl}$, where β_l and α_l are the compressibility and thermal expansion coefficients of the liquid phase and β_{gl} and α_{gl} those of the glass. Analogously the configurational entropy in the Gibbs view is assumed to freeze in at T_g, and has a temperature coefficient $\Delta C_p/T$ above it.[24] Supporters of the free volume theory have proposed other definitions of free volume that allow it to have a temperature dependence below T_g, and consequently a different temperature or pressure dependence above it, than what I have assumed above.[34,35] While this certainly achieves agreement with experiment that is otherwise lacking, it does so at the price of an additional *ad hoc* hypothesis, one that the entropy theory has no need of, and that is not intrinsically plausible. The thermodynamic properties of glasses below T_g are well accounted for in their magnitudes and temperature dependences in the same terms we use for crystals: lattice vibrations with some anharmonicity. It is hard to see why the volume increase as vibration amplitudes get larger is "free" in the same sense that the increase resulting from structural rearrangements in the liquid is.) Third, cold flow in glassy polymers, as well as plasticity in inorganic glasses, has been explained both in terms of models involving stress-assisted thermal activation over energy barriers[36–43] and in terms of free volume.[44–49] It should be mentioned that the Adam–Gibbs theory is a special case of a thermal activation model. I have previously expressed my preference for a thermal activation description,[41,50] but must admit that neither view has yet prevailed. Fourth, the empirical constant T_0 of the Vogel equation is often in good agreement with the temperature at which the extrapolated calorimetric configurational entropy of the liquid vanishes.[25,51]

My own view, on the basis of the above comparison, is that the entropy theory of Gibbs and associates makes the better showing, although the free volume theory appears to be more widely believed in by polymer scientists.

Attempts both to distinguish between the theories and to refine them have been made by comparing the

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various equations with viscosities measured over wider temperature ranges than were originally regarded as their domain of validity.[20,35,52–56] In so doing, the degree of success or failure achieved appears, in my personal and sceptical view, to depend on the extent to which additional adjustable parameters are introduced. Some recent examinations of the Adam–Gibbs equations have used calorimetrically measured entropies, without leading to conclusive support for or refutation of the equation.[51,57,58] Further, recent critical examinations of viscosity data on a large number of liquids of different chemical classes indicates that a single reduced equation will not work for all of them,[59,60] even in a limited range near T_g. Some simple liquids have recently been shown to have a temperature dependence for viscosity of the Arrhenius tpye, over the viscosity range of 10^4–10^{12} poises usually associated with the Fulcher equation[61,62]; these include some liquids having only van der Waals interactions between molecules. A recent study of B_2O_3 in the high viscosity range has shown that although the behavior between 10^2 and 10^{12} poise is well fit by a Fulcher equation, an Arrhenius equation fits from 10^{10} to 10^{14} poise, where the differences between the two equations would be expected to be most striking.[63]

It thus does not appear that when wide ranges of temperature are considered any relatively simple equation, with a small number of parameters whose magnitudes are required to lie within limits set by some physical assumptions as to their significance, will emerge, nor can we expect to distinguish between the free volume and the entropy theories by an appeal to this type of experiment. This is a disappointing conclusion, but one must ask the question, is it so very surprising?

There is every reason to think that the viscosity of a liquid is a property sensitive to fine details of the laws of force between the individual molecules of the liquid, as well as to the presence or absence of internal molecular degrees of freedom. No theory of the crudity and naivete of those discussed here, with a major stress laid on one or another thermodynamic property, itself a gross average over all the complexities of molecular interaction and shape, is going to be anything better than semiquantitative in character.

It would thus seem that for further progress we have no choice but to await the development of a rigorous molecular theory of viscosity. This is a pessimistic conclusion but a reasonable one. However one may ask whether crude theories of the sort we have been discussing do not have a useful role to play in the development of the rigorous molecular theory we hope will some day replace them. The modern molecular approach to viscosity proceeds via the formulation of the shear viscosity (or more precisely the entire linear viscoelastic response) in terms of appropriate integrals over the stress-time correlation function in a fluid.[64,65] There is no difficulty, in principle, in imagining computer experiments generating this correlation function in a finite sample of molecules set into motion according to Newton's laws. It is not yet clear how large a sample of molecules is needed, nor how long a time of study is required, to achieve the equivalent of an infinite number of molecules studied for an infinite time, but one might guess that such a calculation will be within our reach in the immediate future, for liquids having the simplest, spherically symmetric, pair potentials. We may ask what would be the outcome of such a calculation? The degree of confidence we have in the relation between the correlation function and the viscoelastic response is such as to leave no doubt that if the potential of interaction were accurately known, the correct viscosity would automatically be found. Such a calculation may well be regarded as an excellent way of testing whether indeed we do know the potential accurately: is a two-parameter description of the pair potential good enough to calculate the viscosity to within x percent at densities of y? What is the contribution of deviations from pairwise additivity? If this is all we obtain, the applicability of such calculations to more complex molecules becomes uncertain. The more complex a molecule becomes, the more difficult and time consuming the computer calculation will be, partly because of the introduction of many additional degrees of freedom per molecule, and partly because of the greater number of parameters necessary to specify the interaction energy between the molecules. The question is thus raised: Are "rigorous" calculations of the viscosity of complex molecules possible at all in the forseeable future? It appears more likely that even molecular theories of viscosity will be forced to rely on hypotheses or conjectures about molecular motion in liquids: These conjectures will permit approximate calculations, but using the real laws of molecular dynamics. This suggests that rigorous computer calculations on simple atomic liquids will have an additional purpose to that of finding the correct potential of interaction: They will either permit the testing of, or even independently suggest, approximate assumptions about molecular

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motion that will permit the calculation, within acceptable accuracy, of the viscosity of more complex liquids. However, it is likely that the assumptions about molecular motion found suitable for liquid argon, and applicable to ethane or benzene, may not be at all suitable for more complex liquids, in the highly viscous condition near T_g. While the completely general representation of viscosity via the stress-correlation function is just as valid, the assumptions necessary to make calculations based upon it tractable may be of a completely different character from those that are appropriate in the less viscous regime. This suggests an extremely useful role for crude theories of viscosity: those that are found to be successful may suggest directions for more theoretically oriented and rigorous approaches to follow.

Crude theories serve other purposes as well. Although they cannot be expected to be useful for precise quantitative predictions, they can provide the basis for a broad range of qualitative or semiquantitative prediction, permitting relations between apparently different phenomenological properties to be inferred. Further they offer a framework within which to organize large masses of otherwise unrelated observations and data. Also, they can be fruitful in suggesting experiments that might not otherwise be thought of.

Judged by these criteria, as I have noted earlier, the entropy theory stands up better than the free volume theory. However both theories share a certain vagueness of description of the flow process. Some molecular rearrangement of a completely unspecified nature is postulated to be the basic step in viscous flow. These rearrangements are of course occurring all the time in the absence of an external stress; the external stress, by biasing them, reveals their existence, though they can be studied in the absence of stress by other means. The theories concern themselves only with conjectures as to the necessary condition for the occurrence of the rearrangement: either the presence of some free volume in the neighborhood, or the presence of sufficient thermal energy to permit the surmounting of a free energy barrier whose mean height is in turn a function of the configurational entropy density. There is certainly nothing implausible either about the idea of some local expansion being necessary for a molecular rearrangement, or the idea that the smaller the number of configurations avaliable to the liquid, the more cooperative the rearrangement must be. But there are a number of questions one may reasonably ask about the molecular processes of flow that these theories have not attempted to answer.

Some earlier and now discarded or ignored models of the flow process have tried to be more explicit. The activated state theory of Eyring[66] was based on a picture involving the activated jumping of molecules into available holes in a liquid quasilattice. However, while the jumping of molecules into holes may be a plausible description of a diffusive process, there are serious difficulties in the way of understanding it as a mechanism of viscous flow. It has been pointed out that a uniform stress field does not have the requisite symmetry to introduce a bias into such a jump[15,67]; some greater asymmetry than is present in the conventional representation of the process[66] is needed. Attempts to correct this weakness have been made, by replacing a jump into a hole by a rotation of an atomic pair in a slightly expanded region of the liquid[67,68]; however Mooney has pointed out that exactly the same symmetry principle is violated by this model.[69] These theories have of course been more frequently used for liquids composed of molecules quite unlike the billiard balls of the Eyring and Cohen–Turnbull models. One might expect that the lack of symmetry of the molecules, or failing that, the lack of symmetry of the local molecular arrangements, will be sufficient to bias molecular jumps into holes in one way or another. Accepting this would make the Eyring calculation of the force acting on a molecular cross section irrelevant, and also would merely shift the problem without resolving it. There is a difficulty in regarding flow in a liqiud as taking place via the slipping of "lattice planes" past one another. The deformation represented by such a picture includes a rigid body rotation as well as a pure shear strain, but the rotation plays no part in the relation between stress and strain rate. We have a right to demand that the molecular picture represent only a pure shear strain, and once we do, the "lattice planes" cease to be relevant.

Mooney has shown how to represent (in a two-dimensional example) what sort of rearrangements involving spherical molecules and holes could correspond to a pure shear deformation.[69] However his picture has another drawback. The liquid is left after the deformation in an oriented state, and the irreversibility is explained. The reader may verify that this is a general problem for any of the "hole" mechanisms by the following argument. Imagine the shear strain resolved into its principle strains, using these to define a pair (in two dimensions) of Cartesian axes. Then whatever the details of the molecular model, the initial (A) and final (B) states of the rearrangement must be equivalent upon a rotation of 90 degrees. This is necessary to ensure the thermodynamic equivalence of the A and B states. Now consider the liquid as a whole, before shear deformation has occurred. The local molecular configurations must be random, hence as many must be in B states and A states. If the external stress, referred of course to the same principal axes as the strains, biases transitions from A to B states, the liquid ends up with

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more B states than A states. Hence it is oriented, and the deformation has not been irreversible. Some sort of thermal randomization must be invoked to save the situation, but it is precisely the rate and mode of this randomization that is left out of the models. For a hole or free volume mechanism to be complete, not only must the motion of molecules into holes be considered, but also the local appearance and disappearance of holes, which is one possible molecular description of volume relaxation. A little thought will convince the reader that the molecular rearrangements involved in a molecular jump into a hole and those involved in the creation or vanishing of a hole are quite different, the latter seeming to require a much greater cooperative character. Experimentally however the shear and volume relaxation times are almost exactly equal, over wide variations in their absolute values.[15] This in turn suggests that if a hole theory is correct, volume relaxation limits the rate of shear relaxation, and any molecular model must reflect this.

Viscous creep in crystalline solids takes place by a vacancy mechanism,[70,71] but here the surfaces of the crystal act as sources or sinks for vacancies, whose flux is driven by nonuniform stresses.

The models described above have attempted, and to a greater or lesser extent failed, to answer three basic questions about the flow process:

(1) How does the external stress bias a local molecular rearrangement?

(2) How does the local molecular rearrangement give rise to a deformation of a macroscopic sample of liquid?

(3) Why is this deformation irrecoverable?

It is not obvious that there can be any simple, intuitively acceptable answer to these questions. Certainly the history of intuitively simple theories of complicated molecular phenomena suggests that when more rigorous molecular theories have become available, the simple theories are often revealed to have been very poor approximations to the real physics of the problem, and their degree of success either fortuitous or a consequence of parameter adjustment. The unsatisfying vagueness of the free volume and entropy theories may well be the best we can do at the present time.

These reservations notwithstanding, I attempt in what follows to develop a picture of the molecular nature of viscous flow in viscous liquids. I hope first, that this picture will provide intuitively convincing answers, in terms of known laws of physics, to the three questions posed above. Second, I hope that such a picture can also be the first step toward constructing a better, if still crude, theory of viscosity and the glass transition.

II. JUSTIFICATION OF A POTENTIAL ENERGY BARRIER DESCRIPTION

I will begin by an attempt to justify my belief that, when all is said and done, the existence of potential energy barriers large compared to thermal energy are intrinsic to the occurrence of the glassy state, and dominate flow, at least at low temperatures. This is in agreement with the entropy concepts of Gibbs, but not with the free volume viewpoint.

It is a well-known theorem of classical statistical mechanics that given the potential energy U as a function of the atomic coordinates, both the thermodynamics (through the configurational integral)[72] and the transport properties (through the equations of motion) are determined. Like most general theorems, this is not often useful in its unmodified form, as witnessed by the fact that we do not as yet have a rigorous equilibrium statistical mechanical theory of the liquid state, even for spherically interacting molecules whose potential energy is assumed to be a sum of pairwise interactions, nor do we have a theory of viscosity for such liquids.[16,65] However we can come close to an evaluation of the configurational integral in certain special cases, most notably the crystalline solid, where the properties of the potential energy surface take on a particularly simple form. When I speak of the potential energy surface I refer to U plotted as a function of $3N$ atomic coordinates in a $3N+1$ dimensional space. In such a representation the state of a system is represented by a point moving on the surface with a $3N$ dimensional velocity whose average value is temperature dependent. U itself is not a function of temperature, only of coordinates, but the probability distribution for potential energy of a state point of course is, through the Boltzmann factor, $\exp(-U/kT)$, whose integral over all coordinates is the configuration integral. Our ability to evaluate the thermodynamic properties of a crystalline solid lies in the fact that at low temperatures the state point tends to occur almost all the time in the vicinity of a minimum in the U surface. The potential energy U thus can be expressed as a sum of terms quadratic in the small displacements of the atoms from their equilibrium positions. The mechanical stability of the crystal implies that U is a positive definite form in these displacements, which in turn leads to a description of the motion of the state point in terms of harmonic vibrations.

My justification for asserting the importance of potential barriers in the glassy state and in liquids "not too far" from their glass transitions (a phrase I intend to make more precise later) is based on the following five statements:

(1) A glass at low temperatures is, like a crystal, mechanically stable, in the sense that if atoms are dis-

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placed small amounts from their equilibrium positions, there are restoring forces tending to return them to these positions. The potential energy is a positive definite form in these small displacements. We make use of this in our standard assumption that the thermodynamic properties of a glass at very low temperatures are describable in terms of a spectrum of harmonic vibration frequencies. *A glass at low temperatures, like a crystal, is at or near a potential energy minimum.*

(2) We find experimentally that glasses as ordinarily prepared have a finite configuration entropy. Further, we know that the state of a glass at low temperatures, as measured by its energy, its entropy, or any other convenient property, is dependent on the thermalt reatment it has received while passing through the transformation region.[73,74] It follows that *that portion of the potential energy surface that represents the liquid or glassy region has, unlike the portion associated with the crystalline solid, a large number of minima, of varying depths.*

(3) At absolute zero, the state point of a glass will be trapped (ignoring quantum mechanical uncertainty considerations) in some one minimum. *As temperature is raised, sufficient thermal energy ($\frac{1}{2}kT$ per classical kinetic degree of freedom) will become available to allow transitions to take place over potential barriers, even though they are large compared to the thermal energy.* This provides a mechanism both for the attainment of thermodynamic equilibrium and for flow. Under such conditions, either an activated state type of theory, or one much like it, will be the appropriate one for describing deformation.[66]

(4) It should be clear that the nature of potential energy is such that it does not make sense to speak of the potential energy of one molecule in the same way that we can speak of the kinetic energy of one molecule. U is a function of *all* the atomic coordinates. There are certain special situations where it may be useful to treat one molecule by itself, as is done, for example, in the theory of the vacancy mechanism for diffusion in a crystal. There the potential energy for the diffusive step can be defined by a time average over all the atomic motions, with the diffusing atom held fixed. The time varying part of the potential energy may then be separated out as a fluctuating force acting on the diffusing atom. In this discussion however we will not make this factorization. *However we will assume that a transition over a potential barrier in U space is in some sense "local," in that in the rearrangement process leading from one minimum to a "near-by" one, most atomic coordinates change very little, and only those in a small region of the substance change by appreciable amounts.*

As the temperature increases further but is still low enough for the system to be regarded as in or near the glassy state, more than one molecular rearrangement will be occurring in different regions at the same time. Under these conditions, the state point is no longer in a potential minimum most of the time, but it will still be true that it will be near a potential minimum if we consider the atomic displacements in different local regions one at a time, while the atoms in other regions are held fixed. The system will *always* be in the process of transition, rather than some of the time, but always *near* a minimum, in the sense that a sudden cooling will drop it into a minimum with relatively small changes of *most* of the coordinates.

(5) As temperature is raised, a point will be reached where thermal energies will now be comparable to the heights of potential barriers. While the potential energy surface still will, in principle, determine the motion of the state point and hence the transport properties, the particular simplifications in treatment that result from an activated state type of theory, valid only when barrier heights are of the order of 5 kT or greater, are not available to us.[75–77] Some other model of viscous flow will be needed. *The potential barrier description of flow will have a range of validity at low temperatures, but gradually wash out as temperature is raised and the liquid becomes very fluid.* The conditions under which this happens are the subject of a detailed discussion to follow. We note that the more rigorously grounded molecular theories of viscous flow we have at present, for such liquids as liquid argon, attribute the nearly Arrhenius temperature dependence of viscosity not to potential barriers, but to other sources, such as the sensitivity of the radial distribution function to temperature at a certain critical value of the distance.[78]

In the above I have referred to some type of activated or transition state theory as the appropriate one when potential barriers are large compared to kT. In a recent book, *Statistical Mechanical Theories of Transport Processes*,[65] the author, R. Mazo, specifically excludes transition state theory from consideration, on the grounds that it "is not based directly on the fundamentals of statistical mechanics; in particular the Liouville equation plays no role therein." (p. xi). This may be an unduly critical statement, as Mazo is willing to consider Brownian theories of molecular motion, and it has been shown by Kramers and others that these are consistent with a transition state formulation.[75] But at least we are reminded that the theory as formulated by Eyring[66] is an approximate one, based on certain assumptions as to the details of the motion of state points on potential energy surfaces that as yet are neither theoretically derived nor experimentally proved.[75–77] It does not, even given the height of a potential barrier, provide us with a unique prediction of the rate of a

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[73] A. Q. Tool, J. Am. Ceram. Soc. **29**, 240 (1946).

[74] R. O. Davies and G. O. Jones, Advan. Phys. **2**, 370 (1953).

[75] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[76] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill Book Co., New York, 1965), 2nd ed.

[77] H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press Co., New York, 1966).

[78] A. Suddaby, Phys. Chem. Glasses **5**, 155 (1964).

reaction and its temperature dependence. The problem of how rapidly deactivation occurs, after a barrier has been crossed, is not dealt with by the theory, even though it plays a crucial role in determining irreversibility.[16] Even within the framework of the assumptions, a temperature dependence other than of the "Arrhenius" form can arise from such factors as complicated and competing reaction paths, tunneling, etc.[77] In introducing transition state theory here, I am only conjecturing that in whatever rigorous theory of kinetics we will someday have, processes limited by a high potential barrier will share some common simplifications of approach, and the description will not be terribly different from that of transition state theory. If in what follows I have occasion to assume a potential barrier of height E_{act}, a rate of surmounting it proportional to $\exp(-E_{\text{act}}/kT)$ will be taken as a first approximation, without any pretentious pre-exponential factor $(kT/h)\exp(\Delta S_{\text{act}}/R)$ being written. It should of course be noted that this does not necessarily imply that the viscosity itself will obey such an Arrhenius relation, as witnessed by the Adam–Gibbs theory,[25] which deduces a temperature-dependent activation energy from the initial assumptions, and reproduces the WLF equation.[1,17]

The statements I have made above seem to me to be almost trivially obvious. The crucial question of whether they are useful or not is answered only if we know over what temperature range they can be applied. I offer here some ways of estimating this range of validity.

(A) One estimate may be taken from a paper by Zwanzig,[79] where the usefulness of the concept of vibrational excitations in the liquid state is discussed. Zwanzig concludes that vibrations are present in spite of the absence of a regular lattice for the atoms, but when the relaxation time of the structure is such that a "vibration" damps out in a time of the order of one cycle or less, the idea of a "vibration" is vitiated. He concludes therefore that vibrations have meaning in the glassy state, but not in liquid argon, where τ_s, the shear relaxation time, is 10^{-13} sec, of the order of the reciprocal of the Debye frequency. In more viscous liquids, there will be a division between the low frequencies, which will be highly damped, and the higher frequencies which can undergo many vibrations in a time τ_s. We may estimate thus a critical frequency $\nu_c=1/\tau_s$, and ask what contribution to the thermodynamic properties we would have assigned to the frequencies lower than this. On the assumption of a Debye distribution, we find the lower frequencies contribute only to a small proportion. For example frequencies less than $\nu_{\max}/10$ contribute only a few tenths of a percent to the entropy. This would mean that for $\nu_{\max}\sim 10^{13}$ cps, we could use a vibrational method when $\tau_s\geq 10^{-12}$ sec. Of course, we do not know how bad an approximation the Debye spectrum is to that of the glassy lattice, and how serious anharmonic contributions are as the lattice expands. There is no question that this is too optimistic an estimate, but it does suggest an appreciable range of validity above T_g, at which temperature τ_s is the order of 10^3 sec.

(B) The range of validity is intimately connected with the molecular origin of the shear modulus of the liquid. In the glassy state the modulus reflects the fixed positions of the atoms, and is primarily a potential energy modulus, as in crystals. As the temperature is raised, and molecular rearrangements become more and more frequent, the liquid does not lose its high frequency shear rigidity, but the modulus ceases to be simply describable in potential energy terms and must take on an entropic character. There is no reason to expect a discontinuous change in the value at some one temperature; the shear modulus is in fact experimentally found to be a continuous function of temperature.[15] In contrast to the case of a static elastic modulus,[80] no obvious experiment is known to determine the relative contributions of potential energy and of entropy to an infinite frequency modulus. If such an experiment could be devised, it would provide an additional criterion.

(C) To assert that flow represents the dissipation of stored potential energy by molecular rearrangements implies some sequential character: it must be possible to store the potential energy first, before it is dissipated. Let us consider a stress relaxation experiment, which from phenomenological considerations permits a measurement of the steady-state shear viscosity.[1] This experiment is performed by subjecting the surfaces of a body to sudden fixed displacements, after which the stress necessary to maintain these displacements is studied as it decays. But there must always be an initial transient during which the elastic waves set up by the sudden surface displacements propagate through the sample and die away, in the process of creating the initial uniformly stressed state. It should be obvious that unless the transient time τ_t is much shorter than some mean time τ_s of shear stress relaxation, no stress relaxation experiment can be performed. τ_t is given by the ratio of some characteristic dimension l of the sample to the elastic wave velocity β. Thus a sample can be too large to do a stress relaxation experiment on. We can always take smaller samples as relaxation times get short, but there is a natural lower limit set by the smallest amount of liquid that still has the macroscopic phenomenological properties of viscosity, shear modulus, etc. Assuming $\beta\sim 10^5$ cm/sec[14] and the linear dimension of the smallest permissible sample of liquid of the order of 10^{-6} cm, we find as a minimum transient time 10^{-11} sec. A conservative estimate of the smallest τ_s would be one or two orders of magnitude longer than this, or $\tau_s\approx 10^{-9}$ sec. A liquid with a shorter relaxation time cannot store potential energy for subsequent dissipation.

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[79] R. Zwanzig, Phys. Rev. **156**, 190 (1967).

[80] F. T. Wall, *Chemical Thermodynamics* (W. H. Freeman Co., San Francisco, 1965), 2nd ed.

(D) A third estimate may be based on considerations similar to those discussed in (C) above. At finite temperatures, in a macroscopic sample, more than one local region is undergoing rearrangement at any one time. The idea that there is a potential barrier resisting any one rearrangement is intimately connected with the relative fixity in position of the atoms constituting the environment. It is obvious that at high temperatures, the relative rigidity of the lattice is destroyed by too frequent rearrangements, and a potential barrier description is no longer valid. One may make these ideas more precise by again introducing two time scales, the time τ_r to complete a rearrangement once activation has occurred and the shear (or almost identical structural) relaxation time. Unless the surrounding lattice maintains its rigidity long enough for the rearrangement to complete itself, the rearrangement cannot be regarded as involving motion over a potential barrier which owes its existence to that rigidity. To estimate τ_r we need an estimate of the dimensions of the local region involved in such a rearrangement, and we choose 10^{-7} cm arbitrarily. The time such a region retains its extra energy once that energy is received could be inferred from some sort of correlation function for energy $\langle E(0)E(t)\rangle$, where the energy is that concentrated in the degrees of freedom relevant to the reaction. For most rate processes, for example a chemical reaction, one would expect these degrees of freedom to be only a tiny minority of all the degrees of freedom, so that $\langle E(0)E(t)\rangle$ would have no necessary relation to the correlation function for all the degrees of freedom within a small volume, which in turn determines the phenomenological thermal diffusivity κ. This should be less true, however, for this type of less differentiated activated process, and suggests the thermal diffusivity as a measure of the longest possible time the local region has to complete the rearrangement once activation has occurred. Thus $\tau_r \cong l^2/\kappa$. We have estimated l as 10^{-7} cm; typical values of κ in liquids are of order 10^{-3} cm^2/sec, giving $\tau_r \cong 10^{-11}$ sec, and τ_s again of order 10^{-9} sec.

(E) It has been pointed out that the validity of a potential energy minimum model for a liquid implies the existence of two different scale lengths in molecular motion,[3] or equally, two different characteristic times[17]: a molecule must vibrate around a mean position with an amplitude l_0 for a time τ_0, and then jump a distance l_1 in a time τ_1, where l_1 is of the order of a lattice distance. These two distances and times should be clearly resolvable, with $\tau_0 \gg \tau_1$. Thermal neutron scattering can in principle distinguish between "solid"-like molecular motions of this type and those in which there is no sharp distinction between oscillatory and diffusive displacements.[81,82] The experimental and interpretive difficulties are great, and the number of liquids studied over appreciable viscosity ranges is not large. "Solid"-like behavior is seen surprisingly often, even in such low viscosity (~1 centipoise) liquids as water and liquid metals. Some liquids show a transition from "solid"-like to simple diffusive behavior as temperature is raised. This may reflect the validity of some sort of "cage" or cell model of simple liquids near their melting points, the molecule undergoing an oscillatory motion in a relatively constant potential field between the walls of the cage until a momentary structural breakdown permits its escape to a new cage. The Cohen–Turnbull theory, which was proposed as a molecular justification of the free volume concept, is based on a similar description.[18,19] It follows that the existence of the two time scales τ_0 and τ_1 revealed by neutron scattering is only a necessary but not a sufficient condition for the correctness of the idea that the system is usually trapped in or near a potential minimum.

In any event, the critical viscosity inferred from neutron scattering is smaller than that obtained by the other estimates, and as these estimates place only lower limits on this viscosity already, they are confirmed, without being altered, by the results of this technique. Our three estimates, ranging from 10^{-12} to 10^{-9} sec, for the shortest τ_s for validity of a potential energy model, are gratifyingly close, when it is considered that τ_s is a quantity whose experimentally measurable range can be fifteen orders of magnitude. Remembering that these estimates are to be thought of as necessary rather than sufficient criteria, the conservative course is to regard the largest of them, 10^{-9} sec, as setting the lower limit of validity. Assuming infinite frequency shear moduli of liquids as of order 10^{10} dyn/cm^2, this corresponds to a viscosity of 10 poise, low compared to the values of 10^{13} typical of the transition region, but high compared to the 10^{-2} poise common to simple liquids at their melting points.

III. THE MOLECULAR PICTURE OF THE FLOW PROCESS

It is now necessary to consider the mechanism of viscous flow in more detail. Earlier I have criticized the vagueness of the description of the molecular details of the flow process in the free volume and entropy theories. One of the weaknesses of these theories is the absence of any explanation of how stresses applied to the surfaces of the medium are transmitted through it to act on the individual molecules. The hypothesis used here is that in the glassy and highly viscous states the mechanism of transfer is through the stored potential energy of the lattice. The molecular rearrangements giving rise to viscous flow thus dissipate this stored energy.

An excellent description of viscous flow occurring by such a mechanism is given in an article by Orowan.[83]

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[81] A. Sjölander, "Theory of Neutron Scattering by Liquids," in *Thermal Neutron Scattering*, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965), Chap. 7, pp. 291–345.

[82] K. E. Larsson, "Experimental Results on Liquids," in Ref. 81, Chap. 8, pp. 347–411.

[83] E. Orowan, "Creep in Metallic and Non-Metallic Materials," *Proceedings of the First National Congress of Applied Mechanics* (American Society of Mechanical Engineers, New York, 1952), pp. 453–472.

The clarity and physical insight of his description cannot be improved upon, but it is treated in the context of a general treatment of creep in various types of solids and its language is therefore not appropriate to this discussion. In addition there are certain questions Orowan either does not answer or anwers only by implication. I have therefore added certain ideas of my own to his description, particularly that of the long-range strain field (see below), and I have paraphrased Orowan's discussion, rather than quoting him directly in what follows.

Let us first imagine that we have a sample of glass at a very low temperature, where molecular rearrangements occur so infrequently that they can be considered as taking place one at a time. Let us arbitrarily choose some one molecular configuration at a potential minimum as the reference state, and define it to be strain free. Now let us imagine a molecular rearrangement to a nearby potential minimum. We have postulated earlier that the changes in atomic coordinates arising from this rearrangement are localized in the following sense: Of course as a result of the rearrangement *all* the atomic coordinates in the sample will be changed to new equilibrium positions. However the changes will be largest in some local region, and the further away from this local region we move, the smaller these coordinate changes will be. The changes in atomic positions in the local region do not even approximately resemble displacements we might calculate from phenomenological elasticity, but at longer distances the atomic displacements, while of course not being identical with the macroscopic displacement vector, bear the same relation to it as they would if the displacement field were produced by a purely macroscopic deformation of the body. This means that *as far as the long-range strain field is concerned*, the atomic details in the local region of the rearrangement may be replaced by some equivalent set of phenomenological parameters acting as a source function for the field, i.e., a fictitious local set of body forces, a discontinuity of the displacement field, or whatever happens to be convenient.

This approach is the same as that followed in the continuum theory of lattice defects; the reader is referred to review articles by Eshelby[84] and by DeWit[85] for discussions both of its power and its limitations. The replacement of detailed atomic displacements by a phenomenological elastic strain should not be regarded as an approximation, in say the same sense that the use by Debye of the phenomenological viscosity in his theory of the relaxation of dipolar molecules in liquids is an approximation. When used within the limitations on its validity it is exact, for the same reasons that the phenomenological elastic moduli are in principle calculable from the detailed atomic displacements and forces exerted by atoms on each other. Molecular theory is not made unnecessary: it is still needed to calculate (1) what long-range strain field arises from a given molecular rearrangement (2) how far one must be from the local region to be able to use linear phenomenological elastic theory. The philosophy is similar to that used in the theory of transport properties of polymer solutions, where the long-range consequences of the interaction between a polymer segment and the solvent are described by the equations of phenomenological hydrodynamics.[86] The problems of using this approach in an amorphous material are much greater than in a crystal, where the number of distinct kinds of lattice defects is very limited. In a glass, the number of different types of local molecular arrangements is very large, and even the description of the far-field consequences of changes in the local configuration by a phenomenological source function would require that the phenomenological parameters be governed by a probability distribution. Calculations based on molecular force laws will be difficult indeed. Let us disregard these difficulties, and see what consequences can be drawn.

The long-range strain field, with components e_{ij}, has associated with it a stress field σ_{ij}, with the components connected via the usual equations of phenomenological linear elasticity,[87] for example,

$$\sigma_{ij}^{(A)}=2G^{(A)}e_{ij}^{(A)},$$

where the superscript (A) denotes one particular rearrangement from the reference strain-free state, $e_{ij}^{(A)}$ and $\sigma_{ij}^{(A)}$ denote off-diagonal components of the strain and stress fields resulting from the rearrangement, and $G^{(A)}$ denotes the ordinary shear modulus of the material. The reason it bears a superscript (A) will become apparent later on. Initially, let us assume the sample free of surface tractions or pressures. The displacement vector of the strain field produced by the rearrangement will give rise to some deformation of the surface. This deformation will be a complicated function of position, and will not transform a cube of sample into a parallelepiped. However, the deformation will more closely resemble some simple types of macroscopic deformation than others, e.g., it might represent a slight volume expansion together with a shear deformation elongating the sample along a particular diagonal of the cube more nearly than it represents some other types of deformation. It can be said, using Orowan's term, to be "concordant" with the particular simple macroscopic deformation. Now consider the material to have some surface forces applied tending to produce the simple

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[84] J. D. Eshelby, "The Continuum Theory of Lattice Defects," in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press Inc., New York, 1956), Vol. 3, pp. 79–144.

[85] R. DeWit, in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press Inc., New York, 1960), Vol. 10, pp. 249–292.

[86] J. M. Burgers, *Second Report on Viscosity and Plasticity of the Amsterdam Academy of Sciences* (Nordemann Publ. Co., New York, 1938), Chap. 3.

[87] I. S. Sokolnikoff, *Mathematical Theory of Elasticity* (McGraw-Hill Book Co., New York, 1956).

macroscopic deformation described. On the assumption of linear elasticity, the stress fields produced by the surface forces add to the stress fields resulting from the rearrangement. The elastic energy density of the system can be expressed as a volume integral of the square of the sum of the stresses. It is obvious that if the stress fields tend to cancel, the energy is less, and if they reinforce, the energy is greater. This gives a somewhat more precise meaning to the term "concordant." It is now obvious that those molecular rearrangements whose long range stress fields are concordant with an external stress will be energetically biased by that stress and tend to occur more frequently in its presence than otherwise. In other words the system will spend relatively more time in the "rearranged" state than it does in the absence of the stress. The deformation produced by the applied stress is thus determined by the difference between the time averaged shape of the body in the absence of the stress and in its presence, the time averaging being of course equivalent to a weighting by the appropriate Boltzmann factors. (It should not be forgotten that the major part of the potential energy differences between the two configurations is determined by the atomic coordinates in the local region of rearrangement, and is not describable by phenomenological elasticity. It is only the relative biasing of the two minima that can be described in such terms.) The above discussion again follows the lead of the continuum theory of lattice defects: see Eshelby,[84] pp. 80–84.

The above is of course a somewhat detailed justification of the intuitively obvious idea that an external stress can bias some potential energy minima relative to others. However Orowan has raised a question as to whether it describes viscous flow at all. If the stress is removed, the two potential energy minima of the initial and rearranged states are no longer biased. The system will return to the same time average distribution between the two states that it had before the stress was applied. In short, the deformation produced by the biasing influence of the stress on the relative energies of the two potential minima was not viscous flow at all, but a retarded elastic deformation. The reader will recognize that this, in somewhat different language, is the same criticism made earlier of a free volume model of viscous flow due to Mooney.[69]

How then can such molecular rearrangements produce viscous flow? Orowan's answer is that the deformation becomes irrecoverable only if sufficient rearrangements occur so that the "memory" of the initial potential energy minimum is erased. The effect of additional rearrangements in local regions overlapping that of the initial rearrangement is to bring us eventually to new potential energy minima which are "far" on the potential energy surface from the initial minimum, but equivalent to it in depth. It is only the cumulative effect of overlapping" rearrangements that permits the system to move to a new region of the potential energy surface, where it is in an equivalent thermodynamic state to the initial state, but has received a macroscopic deformation. Each rearrangement has a double effect: on the one hand it tends to incorporate irreversibly into the structure of the material the deformations associated with earlier rearrangements; on the other it too represents in part a recoverable strain, which must be converted to irrecoverable strain by rearrangements yet to take place. It should be clear that over and above any "cooperative" character of a local molecular rearrangement, the topological connections of the glassy matrix and the manner in which stress is transmitted through it impose a cooperative character on viscous flow.

While it is not easy to visualize the details of the molecular rearrangements that lead to this required "erasure of memory," it is not hard to indicate how it can be handled phenomenologically. I have earlier written the relation between the stress and strain fields arising from the rearrangement (A), considering for simplicity only one off-diagonal component:

$$\sigma_{ij}^{(A)} = 2G^{(A)}e_{ij}^{(A)}.$$

Subsequent rearrangements taking place in regions sufficiently close to that in which (A) took place must "incorporate" $e_{ij}^{(A)}$ "irreversibly into the structure of the material": they can do this by relaxing $G^{(A)}$, so that the stresses disappear while the strains remain. Hence while $G^{(A)}$ starts out initially as the ordinary shear modulus of the material, it will gradually fall to zero: whence the superscript.

Rearrangements taking place far from a given region can still affect the events in that region through the long range strain fields: the relative bias of the accessible minima is changed. A molecular theory for this will of course be extremely complicated, but a discussion in phenomenological terms might be enlightening. A body subjected to surface forces tending to produce a deformation has within it some stress field, which has its atomic origin in the sum total of the force exerted by the atoms on one side of some arbitrary dividing surface on the atoms lying on the other side. Phenomenological elasticity is concerned with areas of such dividing surfaces large compared to atomic dimensions and small compared to distances over which the stress changes appreciably. However, the forces are there on the atomic scale, and the force with which the body resists the external force is the sum of these atomic forces. If a local rearrangement to a potential minimum that was preferentially biased by the external stress occurs, it is obvious that the atoms in the local region of this rearrangement support less of the stress after it occurred than they did previously. It follows that the atoms elsewhere must support more. The least any model of the flow process must acknowledge is that the extra stress must be supported elsewhere; the next higher approximation would be to treat this as a phenomenological stress concentration problem, with the region just outside that of the rearrangement supporting a larger (but nonuniform) stress than regions further away. This concept has been applied to the phenomenon of cold flow.[41] A description of volume relaxation under the application of a hydrostatic pressure is somewhat easier to visualize than shear deformation, and might more easily lend itself to a simplistic phenomenological description. The stress field around a spherical hole in an elastic medium that has some positive or negative pressure within it is a solved problem in classical elasticity,[87] and this may be used for the long-range strain field associated with the two (high and low volume) states of a local rearrangement. This field does not have a dilational component, and it follows that even in pure volume relaxation, the attainment of equilibrium will be dependent on the shear relaxation time.

IV. CONCLUSIONS AND POSSIBLE EXPERIMENTAL CONSEQUENCES

The above picture is intended to provide a more intuitively satisfying description of viscous flow than others so far proposed. But it is also obviously a more complicated description, and no purpose (except an esthetic one) will have been served by constructing it, unless new experimental consequences can be drawn.

In a subsequent paper I intend to describe a procedure for constructing a multidimensional potential energy surface, sufficiently complicated to approximate the description presented above, but sufficiently simple to lend itself to calculations of certain thermodynamic and rheological properties of viscous liquids and glasses. It should be obvious, on the basis of the foregoing discussion, that a model of this type will not contain features specific to particular glass forming liquids but instead will represent those features shared by all—a sort of lowest common denominator description.

I would like to conclude with some qualitative, but experimentally testable conclusions that can be drawn from the picture proposed.

It is not hard, almost by inspection, to realize that the picture has one immediate consequence: it requires that a retarded elastic deformation always be present as a concomitant of viscous flow. This is phenomenologically equivalent to saying that no liquid (satisfying the conditions of this model) can have a single relaxation time in shear. This represents a crucial experiment: if any liquid shows a single relaxation time in shear in the temperature range of claimed validity, the picture must be wrong. It is often claimed that Tobolsky and Taylor[88] have observed a single relaxation time in shear in a molecular glass made from Galex. This however is not correct: They measured the time-dependent compliance, and found their results could be fit by a single *retardation* time, phenomenologically equivalent to two relaxation times.[67] Even so, the sensitivity of their methods for detecting a spectrum if one is present has been criticized by Plazek and Magill, who argue that creep recovery is to be preferred, and find broad spectra of retardation times in tri-α-naphthyl benzene by this technique.[55] They believe this to be general in molecular glass formers. Acoustic measurements by Litovitz and associates have always found broad spectra as the transition region is approached; they attribute this broadening of the spectrum to a cooperative character required of the individual molecular rearrangements at low free volume.[20,89–92] At higher temperatures, spectra become narrow, often approaching single relaxation times. For B_2O_3, Macedo and Litovitz have found that acoustic data can be fit by a single relaxation time in shear above $T = 800$°C.[90] At this temperature the shear relaxation time is between 10^{-7} and 10^{-8}, one order of magnitude larger than the relaxation time conjectured to be the lower limit of validity for the picture. Zinc chloride also shows a single relaxation time in the range from 300°C to 400°C.[92] The viscosity is about 60 poise at the lower end of this range and $\tau_s = 4\times10^{-9}$ sec. Zinc chloride has not been studied acoustically at lower temperatures, but shows some breadth of the volume retardation spectrum in the transformation range (90–100°C).[93] The experimental distinction between Litovitz' view and that presented here can be made in liquids showing "Arrhenius" viscosity behavior in the high viscosity regime, as these, according to him, should show single relaxation times or narrow spectra, whereas in this view the curvature, or lack of it, in log viscosity versus $1/T$ plots bears no necessary relation to the breadth of the spectrum.

A second consequence is closely related to the first. One may imagine a situation where a macroscopic sample of liquid has been cooled into an essentially rigid condition even though certain local regions have several potential minima still accessible to them at low temperatures. Such islands of mobility within a frozen matrix could give rise to mechanical or dielectric loss phenomena in the glassy condition. This possibility was suggested originally by Orowan,[83] and discussed by Argon[94] in a recent study of delayed elasticity in inorganic glasses. It is an experimental fact that most, but not all, glasses that have been studied show evidence, either by mechanical or dielectric spectroscopy or nuclear magnetic resonance studies, of some molecular mobility that freezes out at temperatures much below T_g. Extensive studies have been made on

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[89] T. A. Litovitz and G. E. McDuffie, J. Chem. Phys. **39**, 729 (1963).

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polymeric[95,96] and on inorganic glasses,[97] but very little as yet on simple molecular glasses.[98–100] Interpretations of these loss phenomena have usually appealed to specific structural features of the molecules of particular glasses, e.g., side-chain motion in polymers, sodium ion motion in silicate glasses, etc. While it is not suggested that any of these molecular explanations need be in error, the possibility that this type of phenomenon may be inherent in the packing together of molecules in an amorphous state, and thus have as much to do with intermolecular as with intramolecular mobility, should not be disregarded.

ACKNOWLEDGMENTS

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Heat Capacity, Transformations, and Thermal Disorder in the Solid Electrolyte $RbAg_4I_5$

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The heat capacity of $RbAg_4I_5$ has been measured in an adiabatic calorimeter between 5 and 340°K. The compound undergoes transformations at 121.8 and at 209°K and exhibits a very sizable configurational heat capacity. The latent heat and entropy changes of the apparently first-order transformation at 121.8°K are 190.9 ± 0.8 cal mole^{-1} and 1.568 ± 0.007 cal deg$^{-1}\cdot$mole^{-1}, respectively. The second transformation appears to be of the lambda type. Upper limits to the heat and entropy changes are 225 cal deg^{-1} and 1.0 cal deg$^{-1}\cdot$mole^{-1}, respectively. The configurational entropy is 10.81 cal deg$^{-1}\cdot$mole^{-1} at 300°K. A residual entropy of 2.25 ± 1.6 cal deg$^{-1}\cdot$mole^{-1} was found. The standard entropy for the compound is 147.07 cal deg$^{-1}\cdot$mole^{-1}. The $\Delta S°$, $\Delta H°$, and $\Delta G°$ of formation are 20.55 ± 2.2 cal deg$^{-1}\cdot$mole^{-1}, -136.2 ± 0.5 kcal mole^{-1}, and -142.3 ± 0.1 kcal mole^{-1}, respectively. The heat capacity is exceptionally high at all temperatures above $\sim$50°K. This is attributed to a continuously increasing disorder among the silver ions as temperature is increased. A simple model for the disordering process based on incompletely filled sets of silver sites with different energy levels is suggested to account for the residual entropy and excess heat capacity.

INTRODUCTION

Rubidium silver pentaiodide is a member of a family of ionic compounds with the composition MAg_4I_5, where M includes Rb, K, and NH_4.[1,2] These compounds are of interest because, like the high-temperature phases of AgI and Ag_2HgI_4, they have a very high ionic conductivity. Although they are thermodynamically unstable below 300, 309, and 305°K, respectively, with respect to decomposition to AgI and M_2AgI_3, $RbAg_4I_5$ may be retained at room temperature and below for indefinite periods of time in a dry atmosphere. Unlike AgI and Ag_2HgI_4, their conductivity remains exceptionally high to very low temperatures. From x-ray structure determination,[3] the conclusion has been drawn that the conductivity is uniquely related to the motion of silver ions over a large number of unoccupied silver sites situated within iodide tetrahedra. The crystal structure at room temperature is cubic with 4 formula weights/unit cell. The arrangement of the I^- ions is similar to that of the Mn atoms in β-Mn and provides 56 iodide tetrahedra per unit cell, which share faces in such a way as to provide diffusion paths for the Ag^+ ions. There are three sets of crystallographically nonequivalent sites for the Ag^+ ions, one eightfold set and two 24-fold sets, making a total of 56 sites for the 16 Ag^+ ions. The ions are not distributed randomly over these sites. In a previous paper[4] we have considered this nonrandom distribution of the silver ions and the resulting configurational energy and entropy. Two low-temperature modifications have been reported.[3] Only the transition to the lowest-temperature phase results

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